

DESCRIPTION

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**TUBE FOR USE IN HEAT EXCHANGER, METHOD FOR MANUFACTURING SAID TUBE,  
AND HEAT EXCHANGER**

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Priority is claimed to Japanese Patent Application No. 2004-35353 filed on February 12, 2004, and U.S. Provisional Application No. 60/545,535 filed on February 19, 2004, the disclosure of which are incorporated by reference in their entireties.

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**Cross Reference to Related Applications**

This application is an application filed under 35 U.S.C. §111(a) claiming the benefit pursuant to 35 U.S.C. §119(e)(1) of the filing date of U.S. Provisional Application No. 60/545,535 filed on February 19, 2004, pursuant to 35 U.S.C. §111(b).

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**Technical Field**

The present invention relates to an aluminum heat exchanger for use in a car air-conditioning refrigeration cycle, a tube for use in such a heat exchanger, and a method for manufacturing such a tube.

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In this disclosure, the wording of "aluminum" is used to mean aluminum and its alloy.

25



### Background Art

The following description sets forth the inventor's knowledge of related art and problems therein and should not be construed as an admission of knowledge in the prior art.

5        As an aluminum heat exchanger for use in a car air-conditioning refrigeration system, the so-called multi-flow type or parallel-flow type heat exchanger is well known. In such heat exchangers, a plurality of flat tubes are arranged in the thickness direction with a fin interposed therebetween, and a pair of headers  
10       are connected to both ends of the tubes in fluid communication.

      In the next generation refrigeration cycle using CO<sub>2</sub> refrigerant which attracts attention recently, since the refrigerant temperature and refrigerant pressure in the circuit become high, high heat-resistant and high pressure-resistant tubes  
15       are used as tubes for heat exchangers such as condensers.

      Conventionally, as such a tube for use in high temperature and high pressure heat exchangers, a tube in which, for example, a tube core is made of Al-Mn series aluminum alloy such as JIS 3003 is widely used.

20       Furthermore, as disclosed in Japanese Patent No. 2528187 (Patent Document 1), Japanese Unexamined Laid-open Patent Publication No. 2000-119784 (Patent Document 2), etc., for the purpose of further improving heat-resistance and pressure-resistance of a heat exchanger tube, it has been proposed to employ  
25       a tube core made of Al alloy material in which Cu is added to the aforementioned Al alloy material.



On the other hand, Japanese Unexamined Laid-open Patent Publication No. H10-265881 (Patent Document 3) discloses a technology in which Al-Si-Cu-Zn series alloy is thermally sprayed on the tube core to form a brazing material layer thereon.

5 In the aluminum alloy material containing Cu as shown in the aforementioned Patent Documents 1 and 2, however, because of the excellent heat resistance and pressure resistance, it is difficult to mold the alloy material, which in turn causes deterioration of the extrusion molding, for example. Therefore,  
10 it was difficult to manufacture a heat exchanger tube with fineness and high precision by extrusion molding.

Furthermore, in the alloy material containing Cu, intergranular corrosion tends to be easily generated at the Cu boundary. Therefore, especially in cases where the Cu content  
15 exceeds 0.05 mass %, corrosion occurs at the early stage, which may cause insufficient corrosion resistance.

Furthermore, the technology disclosed in the aforementioned Patent Document 3 is directed to the technology for forming a low-temperature brazing material layer on a tube, and is different  
20 from the technology for heat resistance, pressure resistance or corrosion resistance. For example, in this Patent Document, since a large amount of Si is contained in the alloy to be thermally sprayed, the large amount of Cu contained in the thermally sprayed Al-Si material on the tube gathers at the fillet as brazing material.  
25 Accordingly, the strength of the tube itself cannot be increased.

The description herein of advantages and disadvantages of



various features, embodiments, methods, and apparatus disclosed in other publications is in no way intended to limit the present invention. Indeed, certain features of the invention may be capable of overcoming certain disadvantages, while still retaining some or all of the features, embodiments, methods, and apparatus disclosed therein.

Other objects and advantages of the present invention will be apparent from the following preferred embodiments.

#### Disclosure of Invention

The preferred embodiments of the present invention have been developed in view of the above-mentioned and/or other problems in the related art. The preferred embodiments of the present invention can significantly improve upon existing methods and/or apparatuses.

The present invention was made in view of the aforementioned problems, and aims to provide a method for easily manufacturing a tube for use in an aluminum heat exchanger excellent in heat resistance, pressure resistance and corrosion resistance by extrusion molding, etc. It also aims to provide a tube for use in such a heat exchanger which can be manufactured by the aforementioned method, and to a heat exchanger using such a tube.

To attain the aforementioned objects, the present invention has the following structure.

[1] A method for manufacturing a tube for use in an aluminum heat exchanger, the method comprising the steps of:



preparing an aluminum flat tube core;

forming a sprayed layer on a surface of the tube core by thermally spraying alloy containing Cu (including its alloy) and Zn (including its alloy), or an alloy containing Cu and Zn, wherein  
5 the sprayed layer contains Cu and Zn and Si content is 2 mass% or less.

In this invention, Cu and Zn adhering to the tube core by thermal spraying will be diffused by the heating at the time of brazing, etc., during the heat exchanger production process, and  
10 a Cu diffusion layer and a Zn diffusion layer will be formed. The heat resistance and pressure resistance of the tube is improved by the Cu diffusion layer, and a sacrificial corrosion layer is formed by the Zn diffusion layer, resulting in sufficient corrosion resistance. When Cu and Zn are diffused, since the range where  
15 Cu diffuses in Al material (tube core material) is small than the range where Zn diffuses in the Al material, Zn is diffused in a larger range as compared with Cu. Thus, a diffusion layer in which a Cu diffusion layer is formed within a Zn diffusion layer (sacrificial corrosion layer) can be formed. Accordingly, the  
20 corrosion of Cu which causes intergranular corrosion will occur within the sacrificial corrosion layer. Thus, durability can fully be maintained without causing substantial deterioration of corrosion resistance.

Furthermore, since Cu and the Zn is thermally sprayed on  
25 the tube core, the Cu content in the tube core can be kept lower. For this reason, high temperature high strength at the time of



forming the material can be prevented by the containing Cu, resulting in easy metal working such as extrusion, which in turn can attain high manufacturing efficiency.

In the present invention, by employing the following structure [2] to [16], the aforementioned functions and effects can be obtained assuredly.

[2] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in the aforementioned Item 1, wherein a Cu adhesion amount of the sprayed layer is adjusted to 1 to 10 g/m<sup>2</sup>.

[3] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in the aforementioned Item 1 or 2, wherein a Zn adhesion amount of the sprayed layer is adjusted to 1 to 20 g/m<sup>2</sup>.

[4] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in any one of the aforementioned Items 1 to 3, wherein an average thickness of the sprayed layer is adjusted to 0.4 to 50  $\mu$ m.

[5] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in any one of the aforementioned Items 1 to 4, wherein the tube core is constituted by aluminum alloy material in which a Cu content is 0.05 mass% or less.

[6] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in any one of the aforementioned Items 1 to 5, wherein the tube core is constituted by Al-Mn series alloy.

[7] The method for manufacturing a tube for use in an aluminum



heat exchanger as recited in any one of the aforementioned Items 1 to 6, wherein the tube core is constituted by JIS 3003 alloy.

[8] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in any one of the aforementioned Items 1 to 7, wherein the tube core is formed by extrusion.

[9] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in any one of the aforementioned Items 1 and 8, wherein the thermal spraying processing is performed by arc thermal spraying.

10 [10] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in any one of the aforementioned Items 1 to 9, wherein the thermal spraying processing is performed by thermally spraying Al-Cu-Zn series alloy.

15 [11] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in any one of the aforementioned Items 1 to 9, wherein the thermal spraying processing is performed by thermally spraying Cu-Zn alloy.

[12] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in any one of the aforementioned 20 Items 1 to 9, wherein the thermal spraying processing includes Cu thermal spraying processing for thermally spraying Cu alloy and Zn thermal spraying processing for thermally spraying Zn.

[13] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in the aforementioned Item 12, 25 wherein the Cu thermal spraying processing and the Zn thermal spraying processing are performed simultaneously.



[14] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in the aforementioned Item 12, wherein the Cu thermal spraying processing and the Zn thermal spraying processing are performed at different time points.

5 [15] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in any one of the aforementioned Items 12 to 14, wherein the thermal spraying processing is performed by thermally spraying Cu alloy and Zn by generating arc using a Cu alloy wire and a Zn wire.

10 [16] The method for manufacturing a tube for use in an aluminum heat exchanger as recited in any one of the aforementioned Items 1 to 15, wherein the thermal spraying processing is performed in inert gas atmosphere

[17] A tube for use in an aluminum heat exchanger, wherein  
15 the tube is manufactured by the method as recited in any one of the aforementioned Items 1 to 16.

With the tube for a heat exchanger of this invention, in the same manner as mentioned above, the tube can be easily manufactured by extrusion, etc., and is excellent in heat resistance,  
20 pressure resistance and corrosion resistance.

[18] An aluminum heat exchanger in which an aluminum tube for use in a heat exchanger tube and a fin are brazed in a combined state, wherein the tube is constituted by the tube for use in an aluminum heat exchanger manufactured by the method as recited in  
25 any one of the aforementioned Items 1 to 16.

With this manufacture method of the aluminum heat exchanger



5 In the heat exchanger as recited in the aforementioned Item  
18, the following structure [19] to [20] can be preferably employed.

[19] The aluminum heat exchanger as recited in the  
aforementioned Item 18, wherein the tube for use in a heat exchanger  
comprises a Cu diffusion layer for pressure resistance and heat  
resistance and a Zn diffusion layer for sacrifice corrosion.

[20] The aluminum heat exchanger as recited in the  
aforementioned Item 19, wherein the Cu diffusion layer is formed  
in the Zn diffusion layer.

[21] A refrigeration cycle in which refrigerant compressed  
15 by a compressor is condensed by a condenser, the condensed  
refrigerant is decompressed by a decompression device, the  
decompressed refrigerant is evaporated by an evaporator and then  
returned to the compressor,

wherein the condenser is constituted by the aluminum heat  
20 exchanger as recited in any one of the aforementioned Items 18  
to 20.

[22] A car air-conditioning device provided with the refrigeration cycle as recited in the aforementioned Item 21.

Effects of the Invention

As mentioned above, according to the manufacture method of



the first aspect of the invention, there is an effect that it is possible to easily manufacture the tube for heat exchangers excellent in heat resistance, pressure resistance and corrosion resistance by extrusion, etc.

5       According to the tube for heat exchangers of the second aspect of the invention, there is an effect that the tube can be easily manufactured by extrusion, etc., and is excellent in heat resistance, pressure resistance and corrosion resistance.

10       According to the heat exchanger of the third aspect of the invention, the heat exchanger is excellent in heat resistance, pressure resistance and corrosion resistance.

      According to the refrigeration cycle of the fourth aspect of the invention, it is excellent in heat resistance, pressure resistance and corrosion resistance.

15       According to the car air-conditioner of the fifth aspect of the invention, it is excellent in heat resistance, pressure resistance and corrosion resistance.

      The above and/or other aspects, features and/or advantages of various embodiments will be further appreciated in view of the following description in conjunction with the accompanying figures. Various embodiments can include and/or exclude different aspects, features and/or advantages where applicable. In addition, various embodiments can combine one or more aspect or feature of other embodiments where applicable. The  
20       descriptions of aspects, features and/or advantages of particular  
25       embodiments should not be construed as limiting other embodiments



or the claims.

### Brief Description of Drawings

Fig. 1 is a front view showing an aluminum heat exchanger  
5 according to an embodiment of the present invention.

Fig. 2 is a partially enlarged perspective view showing a  
brazed portion between a tube and a fin in the heat exchanger  
according to the embodiment of the present invention.

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### Best Mode for Carrying Out the Invention

In the following paragraphs, some preferred  
embodiments of the invention will be described by way of example  
and not limitation. It should be understood based on this  
15 disclosure that various other modifications can be made by those  
in the art based on these illustrated embodiments.

Fig. 1 is a front view showing an aluminum heat exchanger  
1 according to an embodiment of the present invention. As shown  
in this figure, this heat exchanger 1 is used as a condenser for  
20 use in a refrigeration cycle of a car air-conditioner, and  
constitutes the so-called multi-flow type heat exchanger.

In this heat exchanger 1, a plurality of flat heat exchanging  
tubes 2 are horizontally arranged in parallel with their opposite  
ends connected to a pair of hollow headers vertically disposed  
25 in parallel in fluid communication. A corrugated fin 3 is disposed  
between the adjacent tubes 2 and on the outermost tube 2, and a



side plate 10 is arranged on the outside of the outermost corrugated fin 3.

In this heat exchanger 1, the tube 2 is made of aluminum or its alloy (hereinafter simply referred to as "aluminum"), and the fin 3 and the header 4 are made of an aluminum brazing sheet in which brazing material is clad at least on one surface thereof. The tubes 2, the fins 3, the headers 4 and the side plates 10 are provisionally assembled into a heat exchanger assembly, and the provisional heat exchanger assembly is brazed in a furnace to be integrally brazed.

As shown in Fig. 2, the tube 2 includes a tube core made of an aluminum extruded article and a thermally sprayed layer 20 containing Cu (including its alloy) and Zn (including its alloy) formed on at least one surface of the tube core.

As the core material of the tube 2, Al-Mn alloy, e.g., JIS 3003 alloy, excellent in high pressure resistance (high strength) and high heat resistance can be used. As the core material, considering the corrosion resistance, it is preferable to use alloy containing 0.05 mass% or less of Cu.

In this embodiment, the tube core is formed by extruding the aforementioned alloy material.

The thermally sprayed layer 20 formed on the tube core can be formed by making Cu and Zn adhere by thermal spraying processing.

Cu and Zn contained in the thermally sprayed layer 20 are diffused by the heating at the time of integral brazing during the heat exchanger manufacturing process, and form a Cu diffusion



layer and a Zn diffusion layer respectively. In these diffusion layers, the Cu diffusion layer is high in heat resistance and high in pressure resistance, and enhances the heat resistance and the pressure resistance (strength) of the entire tube. On the other hand, the Zn diffusion layer is formed as a sacrificial corrosion layer, improving the corrosion resistance of the tube 2, which in turn improves the durability of the tube 2.

In this embodiment, although a method for thermally spraying Cu and Zn on the surface of the tube core is not especially limited, an arc thermal spraying method can be preferably employed. For example, it can be preferable to employ a method in which a thermal spraying gun of an arc thermal spraying machine is moved along the tube core, or a method for thermally spraying Cu and Zn while rewinding a tube core wound in the shape of a coil. Furthermore, in the case where a tube core is an extruded article, a method in which a thermal spraying is continuously performed by a thermal spraying gun disposed immediately after an extrusion die. Especially, in the case where extrusion and thermal spraying are performed continuously, manufacturing efficiency can be improved.

As for the Cu and Zn thermal spraying, the Cu thermal spraying and the Zn thermal spraying can be performed separately or at different thermal spraying positions, or can be performed simultaneously. Alternatively, alloy containing both Cu and Zn can be thermally sprayed.

In cases where the Cu thermal spraying and the Zn thermal spraying are performed separately, either Cu thermal spraying or



Zn thermal spraying can be performed first. For example, after performing the thermal spraying of Cu alloy onto a tube core by arc thermal spraying, Zn can be thermally sprayed. Alternatively, after performing the thermal spraying of Zn, Cu can be thermally  
5 sprayed.

In cases where Cu thermal spraying and Zn thermal spraying are performed simultaneously, for example, an arc can be simultaneously generated using a Cu wire and a Zn wire to thermally spray pseudo Cu-Zn alloy.

10 In cases where alloy containing Cu and Zn is thermally sprayed, for example, Al-Cu-Zn series alloy can be thermally sprayed with an arc thermal-spraying machine, or Cu-Zn series alloy can be thermally sprayed with a flame-spraying machine.

The aforementioned thermal spraying processing is preferably  
15 performed in inert gas atmosphere (non-oxidizing atmosphere), such as nitrogen gas atmosphere, in order to prevent oxidization of the thermally sprayed layer 20 to be formed on the aluminum material (core material) surface.

The thermally sprayed layer 20 can be formed only on one  
20 side of the tube core, or on both sides, the upper and lower surfaces. Needless to say, when forming a thermally sprayed layer 20 on both tube sides, it is preferable to dispose thermal spraying guns at the upper and lower sides of the tube core.

In this embodiment, the Cu adhesion amount on the tube 2  
25 by thermal spraying processing is preferably adjusted so as to fall within the range of 1 to 10 g/m<sup>2</sup> (including the upper limit



and the lower limit), more preferably 2 to 5 g/m<sup>2</sup>. If the Cu adhesion amount is too low, there is a possibility that it becomes difficult to fully secure heat resistance and pressure resistance. On the other hand, if the Cu adhesion amount is excessive, the potential  
5 of the tube surface (i.e., the Cu diffusion layer) becomes noble with respect to the tube core, resulting in preferential corrosion of the tube core, which causes deterioration of durability.

The Zn adhesion amount to a tube 2 is preferably adjusted to 1 to 20 g/m<sup>2</sup>, more preferably 2 to 12 g/m<sup>2</sup>. If the Zn adhesive  
10 amount is too low, a Zn diffusion layer, i.e., a sacrificial corrosion layer, cannot fully be formed, which may cause deterioration of corrosion resistance. To the contrary, if the Zn adhesion amount becomes excessive, the Zn amount in a sacrificial corrosion layer increases excessively, resulting in early corrosion of the  
15 sacrificial corrosion layer, which in turn causes deterioration of durability.

In this embodiment, it is necessary to adjust the Si content in the thermally sprayed layer 20 to 2 mass % or less, more preferably 0.5 mass % or less. That is, if the Si content is too much, the  
20 thermally sprayed layer may be drawn into the brazed portion, which may cause insufficient strength or insufficient corrosion resistance. For example, when alloy containing Cu and Zn is thermally sprayed onto the tube core using Al-Si-Cu-Zn series alloy in which the Si content is 2 mass % or more, almost all of the Cu  
25 contained in the Al-Si alloy is used as brazing material, resulting in a fillet with high Cu concentration, which makes it difficult



to increase the tube strength.

In the present invention, although metallic elements to be thermally sprayed are mentioned above, the thermally spraying material can contain a small amount of other elements in the un-influential degree as inevitable impurities. For example, Fe can be contained by 0.6 mass% or less.

Furthermore, elements, such as Mn, In, Sn, Ni, Ti and Cr, can be contained in the thermally spraying metallic material so long as they falls within the range which does not exert a harmful influence on brazing performance, etc.

In this embodiment, the ratio of the thermal-spraying area to the entire tube surface is preferably set to 50% or more, more preferably 60% or more. That is, if the area ratio is too low, the Cu and Zn containing area decreases, resulting in insufficient strength and heat resistance, and also resulting in insufficient size of a sacrificial corrosion layer, which in turn makes it difficult to secure appropriate corrosion resistance.

In this embodiment, although the average thickness of the thermally sprayed layer 20 is not specifically limited, it is preferably to adjust so as to have an average thickness of 0.4 to 50  $\mu\text{m}$ , more preferably 0.5 to 20  $\mu\text{m}$ . That is, if it is tried to excessively decrease the thickness of the thermally sprayed layer 20, it becomes difficult to control the adhesion amount of the thermally spraying material, resulting in uneven adhesion amount. Accordingly, there is a possibility that desired performance cannot be obtained. To the contrary, even if it is



tried to form an excessively thick layer, an effect corresponding to the thickness cannot be obtained. Furthermore, it is difficult to form a thermally sprayed layer having a thickness of 50  $\mu\text{m}$  or more.

5           On the other hand, the heat exchanging tube 2 of the  
aforementioned embodiment is used together with other heat  
exchanger components, such as hollow headers 4, corrugated fins  
3 and side plates 10, and assembled into a provisional heat exchanger.  
Thereafter, flux is applied to this provisional assembly and dried.  
10   Then, the provisional assembly is heated in a heating furnace of  
nitrogen gas atmosphere to simultaneously braze the components  
to thereby obtain an integrally brazed heat exchanger.

          In this embodiment, due to the heating at the time of the  
brazing, Cu and Zn contained in the thermally sprayed layer 20  
15   of the tube 2 are diffused to form a diffusion layer as described  
above. At the time of this diffusion, since the range that Cu  
diffuses in the aluminum material (i.e., tube core) is smaller  
than the range that Zn does, Zn is diffused in a larger range as  
compared with Cu, a diffusion layer in which a Cu diffusion layer  
20   is formed in a Zn diffusion layer (sacrificial corrosion layer)  
can be formed. Thus, by the Cu diffusion, the heat resistance and  
strength (pressure resistance) of the tube 2 improves as described  
above, and a sacrificial corrosion layer is formed by the Zn diffusion  
layer. Here, although Cu may cause intergranular corrosion, since  
25   the corrosion occurs in a sacrificial corrosion layer, sufficient  
durability can be attained without causing deterioration of



corrosion resistance. Accordingly, the heat exchanger tube 2 excellent in heat resistance, pressure resistance and outstanding resistance can be obtained.

Accordingly, since the tube 2 is excellent in heat resistance, pressure resistance and durability (corrosion resistance), in this embodiment, the heat resistance, pressure resistance and durability of the entire heat exchanger can be improved.

In this embodiment, since Cu and Zn is thermally sprayed onto the tube core obtained by extrusion, the Cu content in the tube core, i.e., the extruded article, can be controlled as low as possible. For this reason, a raise in strength and temperature of the extrusion material due to the Cu content can be prevented, metal working, such as extrusion molding, can be performed easily, resulting in high manufacturing efficiency.

#### Example

Hereafter, Examples according to the present invention and Comparative Examples for verifying effects of the invention will be explained.

Using extrusion material consisting of Al alloy (Cu: 0.02 mass%, Mn: 1 mass%, balance being Al), a multi-bored flat tube having a width of 16 mm, a height of 3 mm and a thickness of 0.5 mm was extruded with an extrusion machine. On the other hand, thermal spraying guns of an arc thermal spraying machine were disposed at upper and lower sides of the outlet of the extrusion machine to thermally spraying Al-Cu-Zn alloy onto the upper and



lower sides of the extruded tube to thereby form thermal sprayed layers. Thereafter, the tube with thermally sprayed layers (tube for heat exchangers) was cooled in a cooling bath and rolled in a coil shape.

5 As shown in the following Table 1, in the aforementioned thermal spraying processing, the Cu adhesion amount was adjusted to  $0.5 \text{ g/m}^2$  and the Zn adhesion amount was adjusted to  $16 \text{ g/m}^2$ .

Using the aforementioned heat exchanger tubes, a provisionally assembled heat exchanger having the same structure  
10 as that of the aforementioned multi-flow type heat exchanger as explained in the aforementioned embodiment was prepared.

Then, slurry in which flux was suspended in water was sprayed onto the provisionally assembled heat exchanger and dried. Thereafter, the heat exchanger assembly was heated in a heating  
15 furnace in nitrogen gas atmosphere for 10 minutes at  $600^\circ\text{C}$  to perform integral brazing to thereby obtain an aluminum heat exchanger sample.

On the other hand, to a plate  $400 \text{ }\mu\text{m}$  in thickness having the same composition (Cu: 0.02 mass%, Mn: 1 mass%, the balance being Al) as that of the aforementioned tube core, thermal spraying  
20 was performed in the same manner as in the above case. Thereafter, the plate was heated under the same brazing conditions ( $600^\circ\text{C} \times 10 \text{ minutes}$ ) to obtain a plate sample.



Table 1

	Sprayed layer		SWAAT result	High temperature tensile result	Remarks
	Cu adhesion amount (g/m <sup>2</sup> )	Zn adhesion amount (g/m <sup>2</sup> )			
Example 1	0.5	16	○	△	High temp. strength: Normal
Example 2	1	5	◎	○	High temp. strength: Good
Example 3	2	2	◎	○	
Example 4	2	5	◎	○	
Example 5	2	10	◎	○	
Example 6	3	3	◎	○	
Example 7	3	8	◎	○	
Example 8	4	2	◎	○	
Example 9	4	6	◎	○	
Example 10	5	2	◎	○	
Example 11	5	12	◎	○	
Example 12	6	8	◎	○	
Example 13	8	3	◎	◎	
Example 14	8	22	○	◎	
Example 15	10	20	○	◎	
Example 16	12	5	○	◎	Core: slightly corroded

<Examples 2 to 16>

Heat exchanger samples and plate material samples were prepared by the same processing as mentioned above, except that the Cu adhesion amount and Zn adhesion amount were adjusted as shown in Table 1 during the thermal spraying processing.

<Example 17>

In performing thermal spraying, using a Cu alloy wire and a Zn alloy wire as thermal spraying wires, an arc is generated simultaneously to thermally spray pseudo Cu-Zn alloy to thereby form a thermally sprayed layer. At this time, as shown in the



following Table 2, the Cu adhesion amount was adjusted to 2 g/m<sup>2</sup>, and the Zn adhesion amount was adjusted to 4 g/m<sup>2</sup>. Other than the above, heat exchanger samples and plate material samples were prepared in the same manner as in the aforementioned embodiments.

5

Table 2

	Sprayed layer		SWAAT result	High temp. tensile result	Remarks
	Cu adhesive amount (g/m <sup>2</sup> )	Zn adhesive amount (g/m <sup>2</sup> )			
Example 17	2	4	◎	△	High temp. strength: Good
Example 18	2	8	◎	△	
Example 19	5	5	◎	○	
Example 20	5	10	◎	○	
Example 21	7	3	◎	◎	
Example 22	7	16	○	◎	
Example 23	7	0.5	△	◎	
Comp. Ex.	Al-Si-Cu-Zn series alloy thermal spraying Si: 10 mass%, Cu: 4 mass%, Zn: 4 mass%, balance being Al		○	×	High temp. strength: Poor

<Examples 18 to 23>

Heat exchanger samples and plate material samples were prepared by the same processing as in Example 17, except that the Cu adhesion amount and Zn adhesion amount were adjusted as shown in Table 2 during the thermal spraying processing.

<Comparative Example>

In performing thermal spraying processing, a thermal spraying layer was formed by thermally spraying Al-Si-Cu-Zn series alloy (Si: 10 mass%, Cu: 4 mass%, Zn: 4 mass%, balance being Al). Other than the above, heat exchanger samples and plate material samples



were prepared in the same manner as in the aforementioned embodiments.

<Evaluation test>

5       SWAAT (Synthetic sea Water Acetic Acid salt spray Test) was performed to each heat exchanger sample of the aforementioned examples and a comparative example. That is, a cycle of spraying the corrosion test liquid by ASTM D1141 for 0.5 hours and leaving it in a wet condition for 1.5 hours was repeated for 960 hours.

10       The corrosion situation of each sample was observed and the results were shown as follows: "◎" denotes that corrosion remains within a design-criteria range (70 to 150  $\mu\text{m}$ ) in a sacrificial corrosion layer and good corrosion resistance was shown; "o" denotes that although corrosion remains within the design-criteria  
15       range in a sacrificial corrosion layer, and the fin joint remaining ratio after the corrosion test was less than 70%, the fin detaching corrosion resistance due to corrosion was poor; "△" denotes that intergranular corrosion was occurred; and "x" denotes that corrosion largely exceeded the design-criteria range in a  
20       sacrificial corrosion layer, and for example, penetration was occurred. The results are also shown in Tables 1 and 2. The fin remaining rate after corrosion test is represented by a percentage of the joining rate of the sample tube and fin after the corrosion test to that of the sample tube and fin before the corrosion test.

25       Furthermore, the high temperature strength (tensile strength



at 200 °C) of each plate sample of the aforementioned example and comparative example was measured. A standard plate (non-thermally sprayed standard plate) processed in the same manner as mentioned above except that no thermal spraying processing was performed  
5 was prepared, and the high temperature strength (tensile strength in 200 °C) of the standard plate was measured.

The rising rate (strength improvement degree) of the high temperature strength in each plate sample with respect to that in the non-thermally sprayed standard plate was measured by  
10 percentage (%), and the results were shown as follows: "◎" denotes that the improvement degree of the strength of the plate was 10% or more; "○" denotes that the improvement degree was 4% or more but less than 10%; "△" denotes that the improvement degree was 2% or more but less than 4%; "×" denotes that the improvement degree  
15 was less than 2%. The results are shown in Tables 1 and 2.

As will be apparent from Tables 1 and 2, in Examples according to this invention, in the SWAAT and high temperature tensile test, satisfactory results were obtained, and it is understood that they are excellent in corrosion resistance (durability), pressure  
20 resistant and heat resistant.

To the contrary, in the comparative examples, although tolerable evaluation was obtained about corrosion resistance, satisfactory results could not be obtained in respect of high temperature strength (pressure resistance and heat resistance).  
25 This is considered that since Si content in the thermally spraying



metal was large the most of Cu contained in Al-Si was used as brazing material, which causes Cu concentration in the fillets to deteriorate the strength and heat resistance of the tube.

5

### Industrial Applicability

This invention can be applied to an aluminum heat exchanger for use in car air-conditioning refrigeration cycle and the method for manufacturing the tube.

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While the present invention may be embodied in many different forms, a number of illustrative embodiments are described herein with the understanding that the present disclosure is to be considered as providing examples of the principles of the invention and such examples are not intended to limit the invention to preferred  
15 embodiments described herein and/or illustrated herein.

15

While illustrative embodiments of the invention have been described herein, the present invention is not limited to the various preferred embodiments described herein, but includes any and all embodiments having equivalent elements, modifications, omissions, combinations (e.g., of aspects across various embodiments), adaptations and/or alterations as would be appreciated by those in the art based on the present disclosure. The limitations in the claims are to be interpreted broadly based on the language employed in the claims and not limited to examples described in  
20 the present specification or during the prosecution of the application, which examples are to be construed as non-exclusive.

25



For example, in the present disclosure, the term "preferably" is non-exclusive and means "preferably, but not limited to." In this disclosure and during the prosecution of this application, means-plus-function or step-plus-function limitations will only  
5 be employed where for a specific claim limitation all of the following conditions are present in that limitation: a) "means for" or "step for" is expressly recited; b) a corresponding function is expressly recited; and c) structure, material or acts that support that structure are not recited. In this disclosure and during the  
10 prosecution of this application, the terminology "present invention" or "invention" may be used as a reference to one or more aspect within the present disclosure. The language present invention or invention should not be improperly interpreted as an identification of criticality, should not be improperly  
15 interpreted as applying across all aspects or embodiments (i.e., it should be understood that the present invention has a number of aspects and embodiments), and should not be improperly interpreted as limiting the scope of the application or claims. In this disclosure and during the prosecution of this application,  
20 the terminology "embodiment" can be used to describe any aspect, feature, process or step, any combination thereof, and/or any portion thereof, etc. In some examples, various embodiments may include overlapping features. In this disclosure and during the prosecution of this case, the following abbreviated terminology  
25 may be employed: "e.g." which means "for example;" and "NB" which means "note well."